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Crystal and Molecular Structures of $RCH_2CH_2SCH_3$ ($R = OCH_3, SCH_3$)

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The crystal structures of 1-methoxy-2-(methylthio)ethane (MMTE) and 1,2-bis(methylthio)ethane (BMTE), which are liquid materials at room temperature, have been analyzed by X-rays at 143 and 243 K, respectively. The crystal of MMTE belongs to the monoclinic system and the space group is $P2_1/n$. The cell dimensions are; $a=8.416(1)$, $b=7.817(2)$, $c=10.181(2)$ Å, $\beta=113.79(1)^\circ$, and $V=612.8(2)$ Å^3. The MMTE molecule has a TTG conformer, which is different from the most stable one derived from the ab initio molecular orbital calculation on the MP2/6-31G* basis set. The crystal of BMTE belongs to the monoclinic system and the space group is $P2_1/c$. The cell dimensions are; $a=6.549(1)$, $b=5.835(1)$, $c=8.728(1)$ Å, $\beta=97.330(9)^\circ$, and $V=330.7(1)$ Å^3. The BMTE molecule lies on an inversion center and has a GTG′ conformer, which is consistent with the most stable one derived from the ab initio calculation. The relative stability of these crystal structures and the possibility of crystal structures with the other conformers were examined by the molecular mechanics calculation. Trials to make a mixed crystal with MMTE and BMTE were in vain.

1,2-Dimethoxyethane (DME), which is a low-melting-point material (melting point, 215 K), has long been a subject of interest for conformational studies[1—8] as the monomer model of poly(oxyethylene), since it has 10 possible conformers. Conformational studies in the crystalline state as well as in the gaseous, liquid, solution, and amorphous states have been investigated from the infrared and Raman spectroscopies[1] and molecular dynamics.[9] In addition, the crystal structure has been estimated based on a lattice variable molecular dynamics.[9] Recently the crystal structure of DME has been identified and indicates that the conformer of DME is TGT, which is consistent with the results of spectroscopies and molecular dynamics, but is inconsistent with the estimated crystal structure.[10] In this paper, the symbols T, G, and G′ will be used to represent the conformers. The symbol T corresponds to the *trans* conformer, and G and G′ correspond to one and the other of two *gauche* conformers. Three symbols of the sequence indicate the C–X–C–C, X–C–C–S, and C–C–S–C torsion angles, respectively. The TGT conformer involves the tg^+t and tg^-t conformers, which mean the approximate X–C–C–S rotation angles 60 and −60° from the *cis* position.

The two title compounds have one or two sulfur atoms instead of the two oxygen atoms of the DME molecule. The monosubstituted compound is 1-methoxy-2-(methylthio)ethane (MMTE) and the disubstituted compound is 1,2-bis(methylthio)ethane (BMTE). These compounds are also low-melting-point materials and the melting points of MMTE and BMTE are 187 and 284 K, respectively. In addition, MMTE and BMTE have 10 and 14 possible conformers, respectively. The conformational studies in the crystalline state as well as in the gaseous, liquid, solution, and amorphous states have been investigated from infrared and Raman spectroscopies.[2] It was suggested from the observed spectra that some conformers coexist in the gaseous, liquid, and amorphous states for both compounds and the TTG and GTG conformers exist in the crystalline state for MMTE and BMTE, respectively. However, the crystal structures have not been reported because of difficulty in getting single crystals at low temperatures.

Recently a new Weissenberg-type diffractometer with imaging plates was designed and made.[11] The diffractometer, which has a κ-type goniometer for automatic crystal alignment and two imaging plates for recording and reading the intensity data, makes it possible to do rapid data collection. This advantage is very useful for data collection at low temperatures because the data collection may be finished before ice is formed on the crystal surface. In addition, a new cooling system without liquid nitrogen was made and was used to obtain the single crystal on the diffractometer and collect the intensity data.

This paper reports the crystal and molecular structures of the two compounds and compare them with the structures derived from the ab initio molecular orbital and molecular mechanics calculations.

Experimental

Preparation of the Single Crystal. The compounds were synthesized by the method reported previously.[1]

The compound of MMTE was used to fill a 0.7-mm glass capillary, which was mounted on the diffractometer. The liquid sample was cooled down at 0.3 K min^{-1} to 177 K, 10 K below the melting point. When the polycrystals appeared in the capillary, the polycrystalline sample was warmed up to the melting point at 10 K min^{-1}. During this process, care was taken not to melt the tiny crystals completely. After several cycles of heating up and cooling down a cylindrical single crystal was obtained in the glass capillary. The sharp diffraction peaks in the oscillation photograph imply that the single crystal was made in the capillary. Such a crystallization method is called in situ crystallization.[12] The same method was used for the BMTE crystal.

Crystal Structure Analysis. After the oscillation photographs were taken to measure the cell dimensions and identify the crystal orientation, no-screen multilayer Weissenberg measurements were done with the new diffractometer. Weissenberg measurements were done with the coupling constant 1 ° mm^{-1} and the oscillation range 10 ° and without setting up a particular axis. Twenty min are necessary to take a photograph. The crystal data and the experimental details are summarized in Table 1. Both of the structures were solved with the program SHELXS-86,[13] and refined by the full-matrix least squares with the program SHELXL-93.[14] The non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located on a difference Fourier map and refined isotropically. The atomic scattering factors were taken from the International Table for Crystallography.[15] The final atomic parameters and equivalent isotropic temperature factors of MMTE and BMTE are given in Tables 2 and 3, respectively. Lists of the anisotropic temperature factors for non-hydrogen atoms and the observed and calculated structure factors are deposited as Document No. 71037 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Molecular Orbital and Molecular Mechanics Calculations.

Table 1. Crystal Data and Experimental Details for MMTE and DMTE

	MMTE	DMTE
Crystal data		
Chemical formula	$C_4H_{10}OS$	$C_4H_{10}S_2$
Chemical formula weight	106.18	122.24
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	8.4155(12)	6.5485(14)
b/Å	7.817(2)	5.8351(11)
c/Å	10.181(2)	8.7276(14)
β/°	113.791(11)	97.330(9)
V/Å^3	612.8(2)	330.77(11)
Z	4	2
D_x/Mg m^{-3}	1.151	1.227
F(000)	232	132
Radiation type	Mo $K\alpha$	Mo $K\alpha$
Wavelength/Å	0.71069	0.71069
μ/mm^{-1}	0.403	0.675
Temperature/K	143	243
Crystal form	Cylindrical	Cylindrical
Crystal size/mm	$0.7\phi \times 5$	$0.7\phi \times 5$
Crystal color	Transparent	Transparent
Data collection		
Diffractometer	Rigaku R-AXIS-II-CS	Rigaku R-AXIS-II-CS
Monochromator	Graphite	Graphite
Data collection method	Weissenberg	Weissenberg
Absorption collection	None	None
No. of measured reflections	3910	2532
No. of independent reflections	1288	760
No. of reflections observed	1198	692
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$\theta_{\max}$/°	27.62	27.49
Range of h,k,l	$-10 \rightarrow 9$	$-8 \rightarrow 8$
	$-10 \rightarrow 10$	$-7 \rightarrow 7$
	$-13 \rightarrow 12$	$-11 \rightarrow 11$
Refinment		
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.030	0.035
$wR(F^2)$	0.081	0.084
No. of reflections used in refinement	1288	760
No. of parameters	95	48
Weighting scheme	$w = 1/[\sigma^2(F_o^2)+(0.0447P)^2+0.0770P]$ where $P=(F_o^2+2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2)+(0.0399P)^2+0.0394P]$ where $P=(F_o^2+2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	−0.004	0.009
$\Delta\rho_{\max}$/e Å^{-3}	0.156	0.289
$\Delta\rho_{\min}$/e Å^{-3}	−0.125	−0.308
Extinction correction	None	None

Table 2. Positional and Isotropic Thermal Parameters (Å^2) for MMTE
The equivalent isotropic thermal parameter (Å^2) is shown for non-hydrogen atoms.

Atom	x	y	z	U or U_{eq}[a)]
S1	0.95408(4)	0.24500(4)	0.06673(3)	0.0483
O1	0.94401(10)	−0.13230(10)	0.33059(9)	0.0450
C1	1.0715(2)	−0.2218(2)	0.4466(2)	0.0495
C2	1.02045(14)	−0.01159(14)	0.26943(12)	0.0394
C3	0.87627(15)	0.08151(15)	0.15100(13)	0.0426
C4	1.0015(2)	0.4119(2)	0.19934(15)	0.0496
HC1A	1.1367(22)	−0.1471(20)	0.5217(18)	0.063(4)
HC1B	1.0140(21)	−0.3006(21)	0.4817(17)	0.057(4)
HC1C	1.1447(25)	−0.2836(22)	0.4114(19)	0.067(5)
HC2A	1.0904(20)	−0.0709(19)	0.2307(15)	0.050(4)
HC2B	1.0922(18)	0.0649(17)	0.3437(15)	0.046(3)
HC3A	0.7997(18)	0.1336(18)	0.1872(13)	0.047(4)
HC3B	0.8106(20)	0.0053(19)	0.0740(16)	0.056(4)
HC4A	1.0951(23)	0.3808(19)	0.2924(17)	0.062(4)
HC4B	1.0298(24)	0.5095(23)	0.1622(18)	0.075(5)
HC4C	0.8944(25)	0.4382(23)	0.2168(17)	0.072(5)

a) $U_{eq}=(1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 3. Positional and Isotropic Thermal Parameters (Å^2) for BMTE
The equivalent isotropic thermal parameter (Å^2) is shown for non-hydrogen atoms.

Atom	x	y	z	U or U_{eq}[a)]
S1	0.71249(6)	0.02113(7)	0.32204(4)	0.0578
C1	0.5906(2)	−0.0735(3)	0.4857(2)	0.0521
C2	0.8327(3)	0.2809(3)	0.3972(2)	0.0672
H1A	0.6922(27)	−0.0833(34)	0.5776(21)	0.068(5)
H1B	0.5451(26)	−0.2331(36)	0.4592(19)	0.065(4)
H2A	0.7332(34)	0.3987(45)	0.4048(24)	0.088(6)
H2B	0.9141(38)	0.2504(42)	0.4895(25)	0.098(7)
H2C	0.9165(30)	0.3323(41)	0.3220(22)	0.092(6)

a) $U_{eq}=(1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

The ab initio molecular orbital calculation was done with the GAUSSIAN 94[16)] program for each conformer. The geometry of each conformer was optimized with the MP2/6-31G* basis set. The calculated energy includes the zero-point energy.

Molecular mechanics calculations were done with the Cerius2 program for examining the possibilities of the crystal structures with different conformers and estimating the difference in packing energy between the observed and estimated crystal structures. Universal and Dreiding force fields were used. The molecular structures obtained from the ab initio molecular orbital calculation were used and treated as the rigid body during energy minimization.

Results and Discussion

1-Methoxy-2-(methylthio)ethane. The ORTEP[17)] drawing of the molecular structure of MMTE with the numbering atoms and the crystal structure viewed along the b axis are shown in Figs. 1 and 2, respectively. The bond distances, bond angles, and torsion angles are shown in Table 4(a). The MMTE molecule has the TTG conformer in the crys-

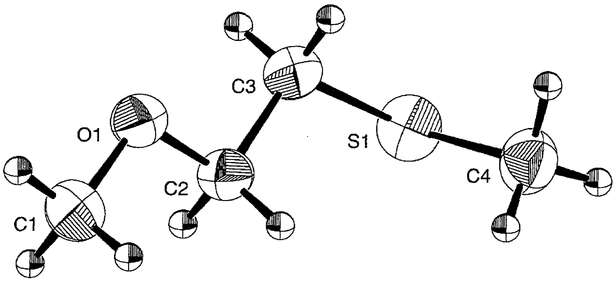

Fig. 1. ORTEP[18)] drawing with the numbering of the atoms for MMTE. Thermal ellipsoids scaled to enclose 50% probability. The spheres of the hydrogen atoms are drawn in an arbitrary scale.

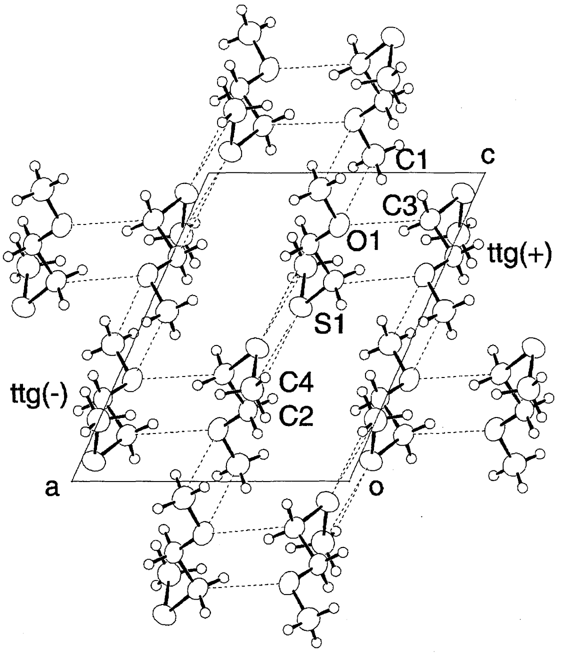

Fig. 2. Crystal structure viewed along b axis for MMTE.

Table 4. Bond Distances (Å), Angles (°) and Torsion Angles (°) for (a) MMTE and (b) BMTE

(a) MMTE			
S1–C4	1.8028(14)	S1–C3	1.8031(13)
O1–C1	1.419(2)	O1–C2	1.4194(14)
C2–C3	1.508(2)		
C4–S1–C3	99.78(6)	C1–O1–C2	111.60(9)
O1–C2–C3	108.10(9)	C2–C3–S1	113.13(8)
C1–O1–C2–C3	−178.06(10)	O1–C2–C3–S1	178.07(7)
C2–C3–S1–C4	−78.55(10)		
(b) BMTE			
S1–C2	1.793(2)	S1–C1	1.809(2)
C1–C1	1.510(3)		
C2–S1–C1	100.74(9)	C1–C1–S1	113.07(15)
C2–S1–C1–C1	70.9(2)	S1–C1–C1–S1	180.0

tal. This result agrees with those by infrared and Raman spectroscopies.[1] The TTG conformer is chiral as observed in the case of DME, therefore the crystal contains two conformers related by a mirror plane. As shown in Fig. 2, the individual conformer lies parallel to the ab plane. The short contacts between intermolecular O and C atoms are closely packed as sheets parallel to the (−1 0 1) plane. The short contacts between oxygen and methylene carbon (O1···C3 = 3.565 Å) and between oxygen and methyl carbon (O1···C1 = 3.614 Å) may be responsible for the sheet formation. Such short contacts as O···CH_2 and O···CH_3 are observed between the same conformers ($ttg^+\cdots ttg^+$ and $ttg^-\cdots ttg^-$) and between the different conformers ($ttg^+\cdots ttg^-$), respectively. The crystal is constructed by a layer structure composed of these sheets. There are short contacts between the layers such as sulfur and methylene carbon (S1···C2 = 3.960 Å) and sulfur and methyl carbon (S1···C4 = 3.935 Å). Since a hydrogen atom of the C–H bond exists between the short contacts of C···O and C···S, the short contacts may be termed hydrogen bonds.

The intramolecular potential energy differences of 13 possible conformers of the MMTE molecule with ab initio molecular orbital calculation at MP2/6-31G* basis set level are shown in Table 5(a), in which the potential energy of the conformer with minimum energy is taken to be zero. The entry for GG′G conformer is missing because of unstability due to the steric repulsion. On the basis of the intramolecular potential energy the most stable conformer is TGG′, which is different from TTG observed in the crystal structure. The TTG conformer is the second most stable one in this calculation. On the other hand, since the population of each conformer depends on the free energy differences, the entropy differences between the conformers are taken into account. For MMTE the entropy of symmetry, $S_{\mathrm{sym}} = -R \ln \sigma$ (σ is the symmetry number characteristic of the point-group symmetry of each conformer), is zero in all conformers and the entropy of the mixing of i components, $S_{\mathrm{mix}} = -R\ \Sigma n_i \ln n_i$, is $R \ln 2$ except for TTT, in which S_{mix} is zero. The obtained free energy differences at each melting point are summarized in Table 5(a). The TGG′ conformer is the most stable even if the entropy is taken into account. Similar phenomenon was observed in the case of DME. Despite the most stable conformer being TTT or TGG′,[4] TGT is the one observed in the crystalline state as shown in Fig. 3. Since the dipole moments of the DME molecules are related head-to-tail in the crystalline state (the dipole moments directly perpendicular to the paper), dipole interaction seems to stabilize the packing. While the energy difference between the observed TGT and most stable TTT conformers for the DME molecule is 2.12 kJ mol^{-1}, the energy difference between the TTG and TGG′ conformers for the MMTE molecule is 2.68 kJ mol^{-1}. The intermolecular interactions should stabilize the packing energy of the MMTE molecules with TTG conformers.

The lattice parameters were not changed when the crystal was cooled at a constant rate of 0.1 K min^{-1} from 187 to 98 K.

Table 5. Intramolecular Potential Energy Differences and Free Energy Differences of (a) MMTE and (b) BMTE at the MP2/6-31G* Basis Set

Energies are given for each conformer relative to the TGG′ and GTG′ conformers for MMTE and BMTE, respectively.

(a) MMTE

Conformer	E (kJ mol^{-1})	ΔG (kJ mol^{-1})
TGG′	0.00	0.00
TTG	2.68	2.68
TTT	5.57	6.64
TGT	6.35	6.35
GGG′	6.55	6.55
TGG	7.11	7.11
GTG′	7.57	7.57
GTG	8.46	8.46
GGT	9.48	9.48
GGG	10.01	10.01
GTT	11.03	11.03
GG′G′	12.83	12.83
GG′T	14.37	14.37

(b) BMTE

Conformer	E (kJ mol^{-1})	ΔG (kJ mol^{-1})
GTG′	0.00	0.00
GTG	0.92	0.92
TTG	2.53	0.89
TTT	4.48	4.48
GGG′	6.77	5.13
TGG	7.70	6.06
GGG	7.83	6.20
TGG′	7.93	6.29
TGT	8.94	7.30

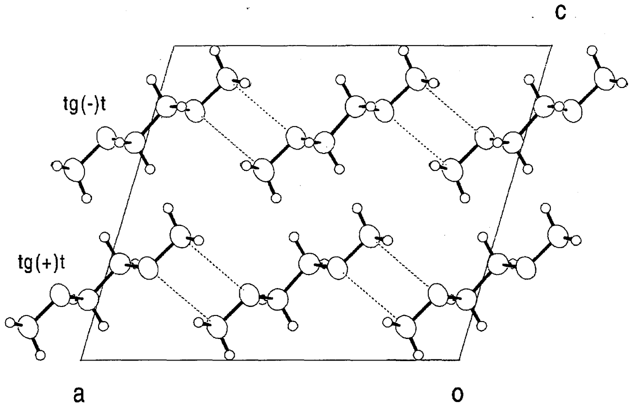

Fig. 3. Crystal structure viewed along *b* axis for DME.[10]

1,2-Bis(methylthio)ethane. The molecular structure with the numbering atoms and the crystal structure of BMTE viewed along the *b* axis are shown in Figs. 4 and 5, respectively. Since the center of the C–C bond of the BMTE molecule is situated on the inversion center, half of the molecule is crystallographically independent. The bond distances, bond angles, and torsion angles are given in Table 4(b). The torsion angles indicate that the BMTE molecule has the GTG′ conformer in the crystal. This result is consistent with those by infrared and Raman spectroscopies.[1] As shown in Fig. 4, BMTE molecules are closely packed

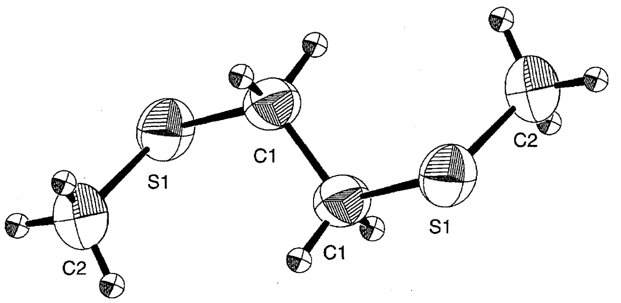

Fig. 4. ORTEP[18] drawing with the numbering of the atoms for BMTE. Thermal ellipsoids scaled to enclose 50% probability. The spheres of the hydrogen atoms are drawn in an arbitrary scale.

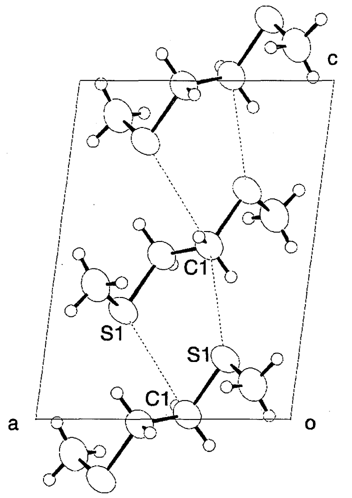

Fig. 5. Crystal structure viewed along *b* axis for BMTE.

as sheets parallel to the *bc* plane and the sheet takes a layer structure along the *a* axis. The short contacts between sulfur and methylene carbon ($S1\cdots C1 = 3.923$ and 3.934 Å) may be responsible for the sheet formation.

Table 5(b) shows the intramolecular potential energy differences of 9 possible conformers of the BMTE molecule. The entry for the GG′G conformer is missing because of unstability due to steric repulsion. For the BMTE molecule the most stable conformer is the GTG′ conformer as shown in Table 5(b) even if the entropy is taken into account ($S_{\mathrm{sym}} = 0$ for TTG, TGG, GTG, TGG′, GTG′, and GGG′ and $S_{\mathrm{sym}} = -R\ln 2$ for TTT, TGT, GGG, and GG′G; $S_{\mathrm{mix}} = 0$ for TTT, $S_{\mathrm{mix}} = R\ln 2$ for TGT, GTG, GTG′, GGG, and GG′G and $S_{\mathrm{mix}} = R\ln 4$ for TTG, TGG, TGG′, and GGG′). Only BMTE among the three compounds (DME, MMTE, and BMTE) takes the most stable conformer estimated from the ab initio molecular orbital calculation. Table 5(b) suggests the following tendencies in the calculation; (1) the SC–CS *trans* conformer is more stable than the *gauche* conformer and (2) the CS–CC *gauche* conformer is more stable than *trans*. The latter factor is observed for MMTE as shown in Table 5(a) and, for ethylmethylsulfide of which the molecule is formed with only the CSCC frame, the *gauche* conformer is stable. Since a similar GTG′ conformer is observed in 1-methylsulfonyl-2-(methylthio)-ethane[18] and 1,2-bis(methylsulfonyl)ethane,[19] the CSCCSC frame is likely to take the GTG′ conformer. However, this may be applied to the case that both of two lone pairs on a sulfur atom are substituted by two oxygen atoms because of the exceptions for 1,2-bis(methylsulfinyl)ethane (TTT)[20] and 1-methylsulfinyl-2-(methylsulfonyl)ethane (TTT).[21] In these compounds only one of two lone pairs on a sulfur atom is substituted by one oxygen atom. Substitutions are made on both sulfur atoms for the former and on one of two sulfur atoms for the later.

The lattice parameters were not changed when the crystals were cooled at a constant rate of 0.1 K min^{-1} from 284 to 98 K.

Packing of Molecules. Although the difference of the molecular formulas among DME, MMTE, and BMTE is only the number of sulfur atoms, the conformers in the crystal structure and the packing of the molecules are quite different among these. This suggests that polymorphic crystals with different conformers may exist. The hypothetical crystal structures were constructed on the basis of the observed crystal structure; i.e. each molecule of three compounds constructs the crystal packings of the other molecules and the intermolecular potential energies were calculated. For example the BMTE molecules with the TGT conformer are packed in the crystal structure of DME (DME type) as shown in Fig. 3. Packing energies are calculated as −83.90 and −101.96 kJ mol^{-1} for Dreiding and Universal force fields, respectively.

Table 6 shows the intermolecular potential energies obtained by assuming the hypothetical crystal structure. Whichever force field is used, the tendency of the relative stability is the same. The BMTE type structure is relatively stable, which reflects on the melting point (284 K) that is the highest among the three compounds (215 K (DME) and 187 K (MMTE)). In addition, this crystal structure is almost the same as 1,2-bis(methylsulfonyl)ethane[21] ($P2_1/c$, $a = 6.260$, $b = 5.949$, $c = 10.643$ Å, $\beta = 90.80°$, $Z = 2$ (the center of molecule lies on the inversion center), mp = 467.0—468.0 K). Although two lone pairs of BMTE are substituted by two oxygen atoms, the molecule of 1,2-bis(methylsulfonyl)-ethane has a GTG′ conformer for the CSCCSC frame. In addition, the molecules are closely packed as sheets parallel to the *bc* plane and the sheet takes a layer structure along the *a* axis as MMTE.

For DME and BMTE the observed crystal structures are the most stable among the structures of three types. For MMTE, however, the BMTE type structure is the most stable. The differences in the intermolecular potential energy between the BMTE and MMTE types are 5.28 and 6.50 kJ mol^{-1} in the Dreiding and Universal force field calculations, respectively. On the other hand, the difference in the intramolecular potential energy between TTG′ and GTG′ conformers for MMTE is 3.47 kJ mol^{-1}. Therefore the crystal structure of the BMTE type is still stable for MMTE even if the energetic disadvantage by taking the GTG′ conformer in the crystal structure is taken into account.

To investigate whether the other conformers appear in crystal structures such as the calculated stable structure, 1 : 1

Table 6. Intermolecular Potential Energies of Each Packings (kJ mol^{-1}) by Using (a) Dreiding Force and (b) Universal Force Field

(a) Dreiding force field

The type of packing	DME (TGT)	MMTE (TTG)	BMTE (GTG′)
DME type	−67.10	−70.29	−83.90
MMTE type	−57.60	−68.08	−77.89
BMTE type	−66.42	−73.36	−86.88

(b) Universal force field

The type of packing	DME (TGT)	MMTE (TTG)	BMTE (GTG′)
DME type (TGT)	−90.03	−88.73	−101.96
MMTE type (TTG)	−76.76	−87.11	−95.66
BMTE type (GTG′)	−86.53	−93.61	−107.34

mixtures of two of the three compounds were crystallized. Crystals of BMTE, BMTE, and DME were grown from the mixtures of BMTE : MMTE = 1 : 1, DME : BMTE = 1 : 1 and DME : MMTE = 1 : 1, respectively. It is clear that the crystal, the melting point of which is higher than another component of the mixed compound, was obtained in every case. These results suggest that there is no conformational polymorph.

For DME the crystal structure have been estimated based on molecular dynamics.[9] In the estimated crystal structure the DME molecule has a TGT conformer and lies on a two-fold axis like the observed one. However the packing is quite different in the C···O interaction. The molecules interact between the same conformers in the observed crystal structure as shown in Fig. 3 (tg$^+$t···tg$^+$t and tg$^-$t···tg$^-$t), but between the tg$^+$t and tg$^-$t conformers in the estimated one. The intermolecular potential energy of the estimated crystal structure were calculated in order to examine which packing is more stable, the observed or estimated crystal structure. The energies of the estimated crystal structure are −69.63 and −90.53 kJ mol^{-1} with Dreiding and Universal force fields, respectively. These values are lower than those of the observed crystal structure shown in Table 6 (−67.10 and −90.03 kJ mol^{-1}, respectively). However, no polymorphic crystal structure has been obtained yet.

Accordingly, the most stable crystal structures of these compounds should be the observed ones after all, even if the calculations indicated the other crystal structure as the more stable phase. In conclusion, the crystal structure analysis of these compounds shows that the C···O and/or C···S interactions predominate in constructing crystal structures when there are not any other strong interactions. Although the conformer in the crystal structure is not the most stable on the basis of the ab initio calculation or is not actually preferable, these interactions should sufficiently decrease the packing energy. Especially, the C···O interactions tend to make a four-membered ring, as shown in Figs. 2 and 3. The ring would be caused by the dipole–dipole interaction between the antiparallel C–O bonds in neighboring molecules. For MMTE, the six-membered ring was formed by the C···S interactions. In order to investigate the most stable crystal structures, such C···O and C···S interactions should be parameterized as well. If these interactions will be taken into account, the packing energy calculation will predict the crystal structures.

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